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BRANCHED AROMATIC POLYCARBONATE AND ITS PRODUCTION METHOD

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【TITLE OF THE INVENTION】

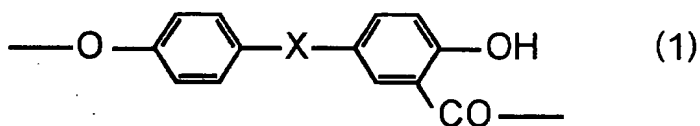
BRANCHED AROMATIC POLYCARBONATE AND ITS PRODUCTION
METHOD

5 【SCOPE OF THE CLAIM(S)】

【Claim 1】

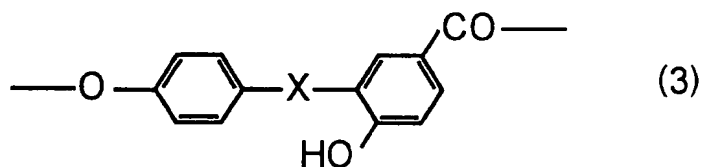
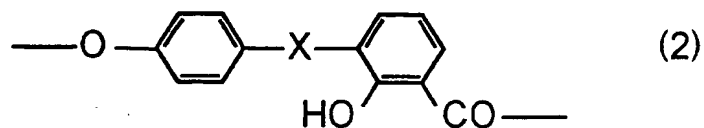
A branched aromatic polycarbonate obtained by
transesterification and having a viscosity average
molecular weight of at least 16,000, wherein the amount
10 of structural units of the following formula (1)
contained in its main chain is within a range of from
3,000 to 10,000 wtpm, and the amounts of structural
units of the following formulae (2) and (3) contained in
its main chain are within a range of from 30 to 5,000
15 wtpm, respectively:

【Ka 1】



wherein X is a single bond, a C₁₋₈ alkylene group, a C₂₋₈
alkylidene group, a C₅₋₁₅ cycloalkylene group, a C₅₋₁₅
20 cycloalkylidene group or a member selected from bivalent
groups represented by -O-, -S-, -CO-, -SO- and -SO₂-,

【Ka 2】

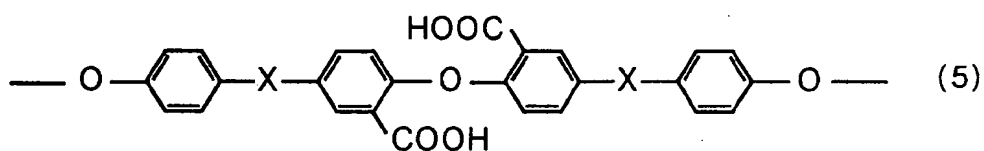
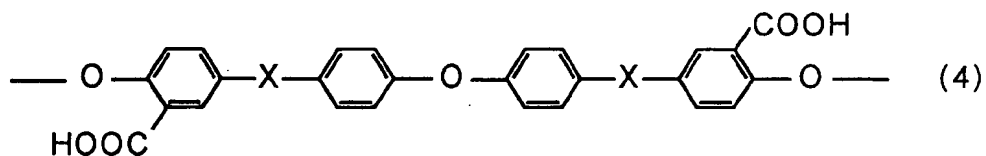


In the formulae (2) and (3), X is a single bond, a C₁₋₈ alkylene group, a C₂₋₈ alkylidene group, a C₅₋₁₅ cycloalkylene group, a C₅₋₁₅ cycloalkylidene group or a member selected from bivalent groups represented by -O-, -S-, -CO-, -SO- and -SO₂-.

【Claim 2】

The branched aromatic polycarbonate according to Claim 1, wherein the total amount of structural units of the following formulae (4) and (5) contained in its main chain is within a range of from 10 to 3,000 wtpm:

【Ka 3】

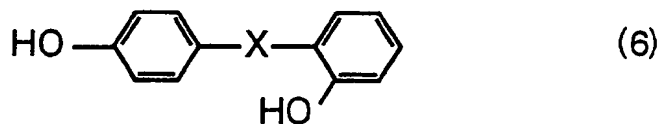


In the formulae (4) and (5), X is a single bond, a C₁₋₈ alkylene group, a C₂₋₈ alkylidene group, a C₅₋₁₅ cycloalkylene group, a C₅₋₁₅ cycloalkylidene group or a member selected from bivalent groups represented by -O-,
5 -S-, -CO-, -SO- and -SO₂-.

[Claim 3]

A method for producing the branched aromatic polycarbonate as defined in Claim 1 or 2, which comprises reacting a carbonic acid diester with an aromatic
10 dihydroxy compound to produce an aromatic polycarbonate, wherein an aromatic dihydroxy compound containing a 2,4'-bisphenol compound of the following formula (6) in an amount of from 100 to 10,000 wtppm is used:

[Ka 4]



15 wherein X is a single bond, a C₁₋₈ alkylene group, a C₂₋₈ alkylidene group, a C₅₋₁₅ cycloalkylene group, a C₅₋₁₅ cycloalkylidene group or a member selected from bivalent groups represented by -O-, -S-, -CO-, -SO- and -SO₂-.

20 **[Claim 4]**

The method for producing the branched aromatic polycarbonate according to Claim 3, wherein the 2,4'-bisphenol compound is 2,4'-dihydroxydiphenyl-2,2-propane.

【DETAILED DESCRIPTION OF THE INVENTION】

【Technical Field to which the Invention Belongs】

The present invention relates to a branched aromatic polycarbonate excellent in quality and its production method. More particularly, it relates to a branched aromatic polycarbonate having improved melt properties and further having improved hue and residence stability, and its production method.

【Prior Art】

10 Production of an aromatic polycarbonate by polycondensation of an aromatic dihydroxy compound and a carbonic acid diester, so-called transesterification is not only relatively simple as compared with a phosgene method (interfacial polymerization method) and is superior in view of operation and cost, but also reevaluated in recent years from the viewpoint of environmental protection since no halogen type solvent such as phosgene or methylene chloride which is highly toxic is used.

20 However, the transesterification has several drawbacks in view of physical properties as compared with the phosgene method, and thus it is scarcely employed as a large scale industrial process. A polycarbonate obtained by the transesterification, as a representative example, has such problems that branches are likely to form, fluidity and moldability tend to decrease, and it is poor in hue of the product, as compared with a product

obtained by the phosgene method.

Several proposals have been made to overcome these problems. For example, a method for obtaining an aromatic polycarbonate excellent in hue, hue stability
5 and heat stability at the time of molding, by making the contents of an isomer and a derivative in the aromatic dihydroxy compound used as a material to be within specific ranges (JP-A-8-104747, JP-A-8-104748, JP-A-8-277236), a method for obtaining a polycarbonate having
10 less branches, by making the phenoxybenzoic acid content in the main chain to be a specific amount with a specific catalyst under a specific reaction condition (JP-A-7-18069, JP-A-8-109251, JP-A-9-278877), or a method for obtaining a less colored polycarbonate by making the p-
15 hydroxyacetophenone content to be at most a specific amount (JP-A-8-27263) may, for example, be mentioned. Such methods are methods proposed to overcome conventional problems and to decrease formation of branches and to improve the hue.

20 On the other hand, a commonly employed aromatic polycarbonate has a linear molecular structure, and a polycarbonate having such a molecular structure may be poor in e.g. melt elasticity and melt strength at the time of melt molding, and their improvements have been
25 desired. Actually, as a method for improving melt properties such as melt elasticity and melt strength of such a polycarbonate, a method for branching a

polycarbonate by an interfacial polymerization method by using a polyfunctional compound such as 1,1,1-tris(4-hydroxyphenyl)ethane (THPE) or 1,3,5-tris(4-hydroxyphenyl)benzene as a branching agent together with
5 2,2-bis(4-hydroxydiphenyl)propane (hereinafter referred to simply as "bisphenol A" or "BPA") has conventionally been known (JP-B-44-17149, JP-B-47-2918, JP-A-2-55725, JP-A-4-89824).

However, an aromatic polycarbonate has a high melt
10 viscosity even if it has a linear structure, and further, a polycarbonate having a branched structure introduced by copolymerization with a polyfunctional compound has a higher melt viscosity and a decreased fluidity. Of such a polycarbonate having a high melt viscosity and being
15 poor in fluidity, the molding conditions may be limited, or molding unevenness occurs, whereby it is difficult to stably obtain a uniform molded product.

In order to overcome these problems, various attempts have been done on a melt polymerization method
20 employing a carboxylic acid diester and an aromatic dihydroxy compound, however, a branching agent may undergo e.g. decomposition at a high temperature, whereby no effect of branching is obtained, and further, it may cause coloring, and accordingly no satisfactory results
25 have been obtained (JP-A-4-89824, JP-A-6-136112, JP-B-7-37517, JP-B-7-116285).

【Problems that the Invention is to Solve】

The present invention is to provide a method for producing a branched aromatic polycarbonate excellent in quality. More particularly, it is to provide a branched aromatic polycarbonate having improved melt properties and further having improved hue and residence stability, and a method for producing such a branched aromatic polycarbonate efficiently.

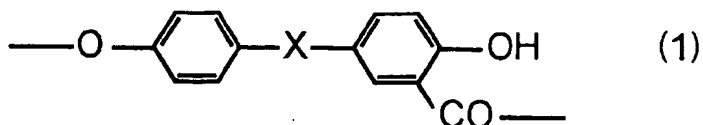
【Means of Solving the Problems】

The present inventors have conducted extensive studies to provide a branched aromatic polycarbonate excellent in hue and excellent in melt properties such as melt strength, and as a result, found that a branched aromatic polycarbonate having specific structural units in its main chain in a specific amount has an improved fluidity under a high load, and has improved hue and residence stability. The present invention has been accomplished on the basis of these discoveries.

Namely, the gist of the present invention resides in providing a branched aromatic polycarbonate obtained by transesterification and having a viscosity average molecular weight of at least 16,000, wherein the amount of structural units of the following formula (1) contained in its main chain is within a range of from 3,000 to 10,000 wtppm, and the amounts of structural units of the following formulae (2) and (3) contained in its main chain are within a range of from 30 to 5,000

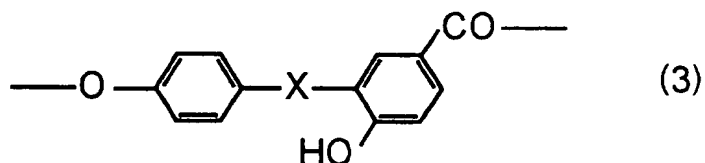
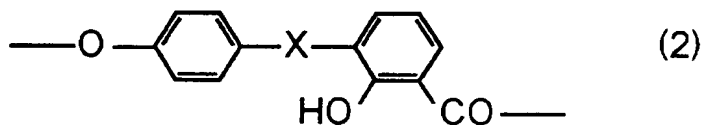
wtppm, respectively:

【Ka 5】



wherein X is a single bond, a C₁₋₈ alkylene group, a C₂₋₈ alkylidene group, a C₅₋₁₅ cycloalkylene group, a C₅₋₁₅ cycloalkylidene group or a member selected from bivalent groups represented by -O-, -S-, -CO-, -SO- and -SO₂-,

【Ka 6】

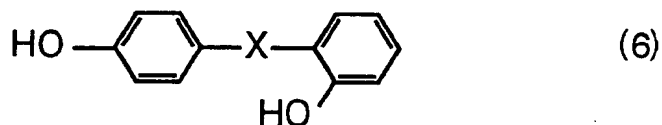


10 In the formulae (2) and (3), X is a single bond, a C₁₋₈ alkylene group, a C₂₋₈ alkylidene group, a C₅₋₁₅ cycloalkylene group, a C₅₋₁₅ cycloalkylidene group or a member selected from bivalent groups represented by -O-, -S-, -CO-, -SO- and -SO₂-.

15 Another gist of the present invention resides in providing a method for producing the branched aromatic polycarbonate as defined in Claim 1, which comprises reacting a carbonic acid diester with an aromatic

dihydroxy compound to produce an aromatic polycarbonate, wherein an aromatic dihydroxy compound containing a 2,4'-bisphenol compound of the following formula (6) in an amount of from 100 to 10,000 wtpm is used:

5 【Ka 7】



In the formula (6), X is a single bond, a C₁₋₈ alkylene group, a C₂₋₈ alkylidene group, a C₅₋₁₅ cycloalkylene group, a C₅₋₁₅ cycloalkylidene group or a member selected from bivalent groups represented by -O-, -S-, -CO-, -SO- and -SO₂-.

【Mode of Carrying out the Invention】

Now, the present invention will be explained in detail below.

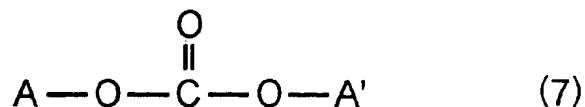
15 Method for producing an aromatic polycarbonate

The aromatic polycarbonate of the present invention can be obtained by melt polycondensation by using an aromatic dihydroxy compound and a carbonic acid diester as materials in the presence of a transesterification catalyst.

Carbonic acid diester

The carbonic acid diester used in the present invention is represented by the following formula (7):

5 【Ka 8】



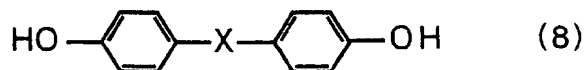
In the formula (7), each of A and A' is a C₁₋₁₈ aliphatic group or a substituted aliphatic group, or an aromatic group or a substituted aromatic group, and A and A' may be the same or different.

The carbonic acid diester of the above formula (7) may, for example, be a dialkyl carbonate compound such as dimethyl carbonate, diethyl carbonate or di-t-butyl carbonate, diphenyl carbonate or a substituted diphenyl carbonate such as ditolyl carbonate. Preferred is diphenyl carbonate or a substituted diphenyl carbonate, particularly preferred is diphenyl carbonate. Such carbonic acid diesters may be used alone or as a mixture of at least two.

Aromatic dihydroxy compound

The aromatic dihydroxy compound used in the present invention is usually represented by the following formula (8):

20 【Ka 9】



In the formula (8), X is a single bond, a C₁₋₈ alkylene group, a C₂₋₈ alkylidene group, a C₅₋₁₅ cycloalkylene group, a C₅₋₁₅ cycloalkylidene group or a

member selected from bivalent groups represented by -O-,
-S-, -CO-, -SO- and -SO₂-.

The aromatic dihydroxy compound of the above formula
(8) may, for example, be a bisphenol such as bisphenol A,
5 bis(4-hydroxydiphenyl)methane, 2,2-bis(4-hydroxy-3-
methylphenyl)propane, 2,2-bis(4-hydroxy-3-t-
butylphenyl)propane, 2,2-bis(4-hydroxy-3,5-
dimethylphenyl)propane, 2,2-bis(4-hydroxy-3,5-
dibromophenyl)propane, 4,4-bis(4-hydroxyphenyl)heptane or
10 1,1-bis(4-hydroxyphenyl)cyclohexane; a biphenol such as
4,4'-dihydroxybiphenyl, 3,3',5,5'-tetramethyl-4,4'-
dihydroxybiphenyl; bis(4-hydroxyphenyl)sulfone, bis(4-
hydroxyphenyl)sulfide, bis(4-hydroxyphenyl)ether or
bis(4-hydroxyphenyl)ketone. Particularly preferred is
15 bisphenol A. Such dihydroxyaryl compounds may be used
alone or as a mixture of at least two.

For production of the aromatic polycarbonate in the
present invention, usually bisphenol A is used as the
aromatic dihydroxy compound, and diphenyl carbonate is
20 used as the carboxylic acid diester. Diphenyl carbonate
is used in an amount of from 1.01 to 1.30 mol, preferably
from 1.02 to 1.20 per 1 mol of the bisphenol A.

Transesterification catalyst

In the present invention, as the transesterification
25 catalyst, an alkali metal compound and/or an alkaline
earth metal compound is used. A basic compound such as a
basic boron compound, a basic phosphorus compound, a

basic ammonium compound or an amine type compound may be used together supplementarily, but it is particularly preferred to use an alkali metal compound and/or an alkaline earth metal compound alone.

5 The alkali metal compound may, for example, be sodium hydroxide, potassium hydroxide, lithium hydroxide, cesium hydroxide, sodium hydrogencarbonate, potassium hydrogencarbonate, lithium hydrogencarbonate, cesium hydrogencarbonate, sodium carbonate, potassium carbonate,
10 lithium carbonate, cesium carbonate, sodium acetate, potassium acetate, lithium acetate, cesium acetate, sodium stearate, potassium stearate, lithium stearate, cesium stearate, sodium borohydride, potassium borohydride, lithium borohydride, cesium borohydride,
15 phenylated sodium boron, phenylated potassium boron, phenylated lithium boron, phenylated cesium boron, sodium benzoate, potassium benzoate, lithium benzoate, cesium benzoate, disodium hydrogenphosphate, dipotassium hydrogenphosphate, dilithium hydrogenphosphate, dicesium
20 hydrogenphosphate, disodium phenylphosphate, dipotassium phenylphosphate, dilithium phenylphosphate, dicesium phenylphosphate, an alcoholate or a phenolate of sodium, potassium, lithium or cesium, or disodium salt, dipotassium salt, dilithium salt or dicesium salt of
25 bisphenol A.

 The alkaline earth metal compound may, for example, be calcium hydroxide, barium hydroxide, magnesium

hydroxide, strontium hydroxide, calcium hydrogencarbonate,
barium hydrogencarbonate, magnesium hydrogencarbonate,
strontium hydrogencarbonate, calcium carbonate, barium
carbonate, magnesium carbonate, strontium carbonate,
5 calcium acetate, barium acetate, magnesium acetate,
strontium acetate, calcium stearate, barium stearate,
magnesium stearate or strontium stearate.

Specific examples of the basic boron compound
include sodium salt, potassium salt, lithium salt,
10 calcium salt, barium salt, magnesium salt and strontium
salt of tetramethyl boron, tetraethyl boron, tetrapropyl
boron, tetrabutyl boron, trimethylethyl boron,
trimethylbenzyl boron, trimethylphenyl boron,
triethylmethyl boron, triethylbenzyl boron,
15 triethylphenyl boron, tributylbenzyl boron,
tributylphenyl boron, tetraphenyl boron, benzyltriphenyl
boron, methyltriphenyl boron or butyltriphenyl boron.

The basic phosphorus compound may, for example, be
triethylphosphine, tri-n-propylphosphine,
20 triisopropylphosphine, tri-n-butylphosphine,
triphenylphosphine, tributylphosphine or a quaternary
phosphonium salt.

The basic ammonium compound may, for example, be
tetramethylammonium hydroxide, tetraethylammonium
25 hydroxide, tetrapropylammonium hydroxide,
tetrabutylammonium hydroxide, trimethylethylammonium
hydroxide, trimethylbenzylammonium hydroxide,

trimethylphenylammonium hydroxide, triethylmethylanmonium
hydroxide, triethylbenzylanmonium hydroxide,
triethylphenylanmonium hydroxide, tributylbenzylanmonium
hydroxide, tributylphenylanmonium hydroxide,
5 tetraphenylanmonium hydroxide, benzyltriphenylanmonium
hydroxide, methyltriphenylanmonium hydroxide or
butyltriphenylanmonium hydroxide.

The amine type compound may, for example, be 4-
aminopyridine, 2-aminopyridine, N,N-dimethyl-4-
10 aminopyridine, 4-diethylaminopyridine, 2-hydroxypyridine,
2-methoxypyridine, 4-methoxypyridine, 2-
dimethylaminoimidazole, 2-methoxyimidazole, imidazole, 2-
mercaptoimidazole, 2-methylimidazole or aminoquinoline.

The transesterification catalyst is used usually in
15 an amount of from 1×10^{-8} to 1×10^{-5} mol per 1 mol of the
bisphenol A, preferably from 1×10^{-7} to 8×10^{-6} ,
particularly preferably from 3×10^{-7} to 2×10^{-6} . If its
amount is smaller than the above lower limit,
polymerization activity required for production of a
20 polycarbonate having a desired molecular weight can not
be obtained, and if its amount is larger than the above
range, the polymer hue tends to deteriorate, and the
amount of foreign matters due to generation of gel tends
to increase.

25 The transesterification reaction is carried out in a
multi-stage process comprising at least two stages.
Specifically, the reaction at the first stage is carried

out at a temperature of from 140 to 260°C, preferably from 180 to 240°C for from 0.1 to 10 hours, preferably from 0.5 to 3 hours. Then, the reaction temperature is increased while gradually lowering the pressure in the reaction system, and the polycondensation reaction is carried out under a reduced pressure of at most 133 Pa at a temperature of from 240 to 320°C finally.

The manner of the reaction may be batch system, continuous system or a combination of the batch system and the continuous system, and the apparatus used may be in any form of a tank type, a tube type or a tower type.

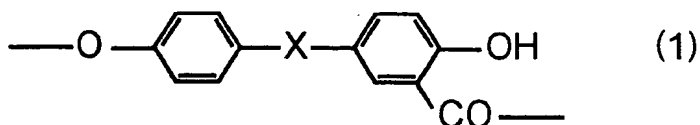
Branched aromatic polycarbonate

The branched aromatic polycarbonate of the present invention is required to have a viscosity average molecular weight of at least 16,000. One having a viscosity average molecular weight less than 16,000 is not preferred since its mechanical strength such as impact strength tends to decrease. The viscosity average molecular weight is preferably within a range of from 16,000 to 60,000 in view of mechanical strength. Particularly, it is suitable to be within a range of from 18,000 to 50,000.

Further, the amount of structural units of the following formula (1) contained in the main chain of the branched aromatic polycarbonate of the present invention is required to be within a range of from 3,000 to 10,000 wtpm, preferably from 3,100 to 9,000 wtpm, more

preferably from 3,200 to 8,000 wtppm.

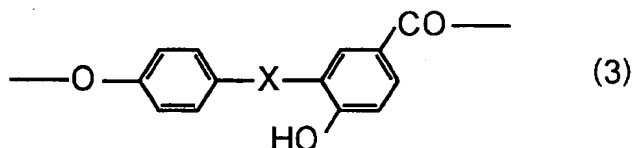
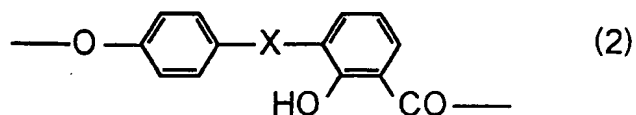
【Ka 10】



In the formula (1), X is a single bond, a C₁₋₈ alkylene group, a C₂₋₈ alkylidene group, a C₅₋₁₅ cycloalkylene group, a C₅₋₁₅ cycloalkylidene group or a member selected from bivalent groups represented by -O-, -S-, -CO-, -SO- and -SO₂-. If the amount of the structural units of the formula (1) exceeds 10,000 wtppm, gel of the produced aromatic polycarbonate is likely to form, such being unfavorable, and further, the hue tends to deteriorate. On the other hand, if it is less than 3,000 wtppm, no intended melt properties by branching will be obtained.

Further, the amounts of the structural units of the following formulae (2) and (3) contained in the main chain of the branched aromatic polycarbonate of the present invention are preferably within a range of from 30 to 5,000 wtppm, respectively, and more preferably from 50 to 4,000 wtppm, respectively:

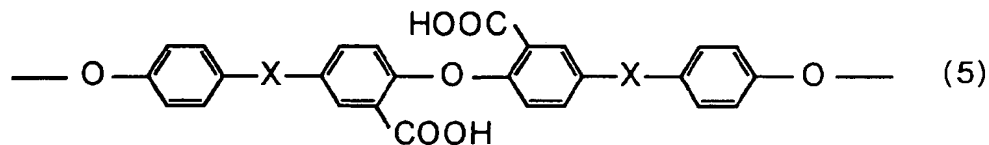
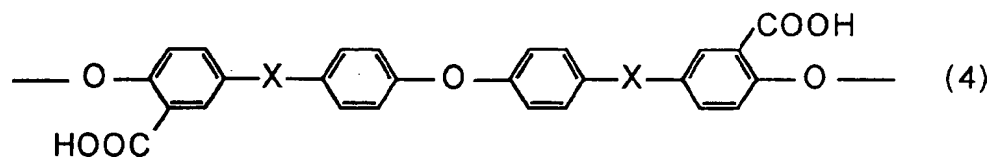
【Ka 11】



In the formulae (2) and (3), X is a single bond, a C₁₋₈ alkylene group, a C₂₋₈ alkylidene group, a C₅₋₁₅ cycloalkylene group, a C₅₋₁₅ cycloalkylidene group or a member selected from bivalent groups represented by -O-, -S-, -CO-, -SO- and -SO₂-. If the amounts of the structural units of the formulae (2) and (3) exceed 5,000 wtpm, branching tends to be too excessive, gelation tends to proceed, whereby molding of the polymer tends to be difficult, such being unfavorable, and further, the hue tends to deteriorate. On the other hand, if they are less than 30 wtpm, fluidity under a high load will not increase, and no intended melt properties by branching will be obtained.

Further, in the present invention, usually structural units of the following formulae (4) and (5) are present in the main chain. Their total amount is preferably within a range of from 10 to 3,000 wtpm, more preferably from 30 to 2,500 wtpm:

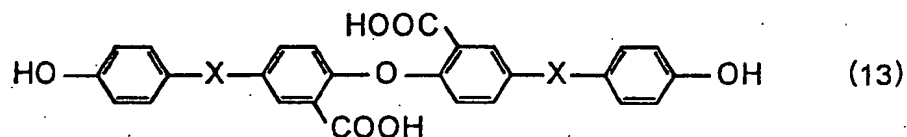
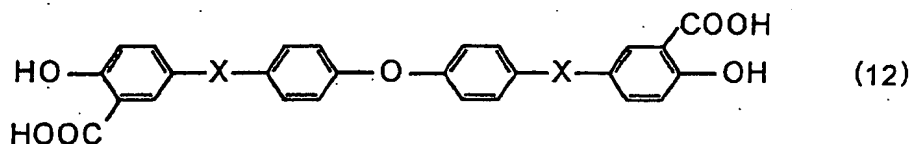
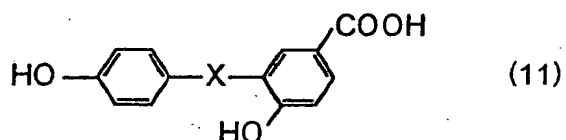
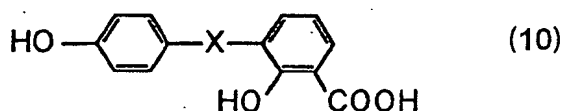
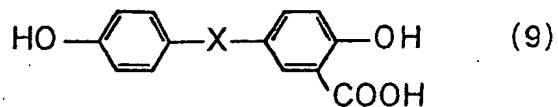
【Ka 12】



- In the formulae (4) and (5), X is a single bond, a C₁₋₈ alkylene group, a C₂₋₈ alkylidene group, a C₅₋₁₅ cycloalkylene group, a C₅₋₁₅ cycloalkylidene group or a member selected from bivalent groups represented by -O-, -S-, -CO-, -SO- and -SO₂-. If the total amount of the structural units of the formulae (4) and (5) exceeds 5,000 wtpm, branching tends to be too excessive, gelation tends to proceed, and molding of the polymer tends to be difficult, such being unfavorable, and further, the hue tends to deteriorate. On other hand, if it is less than 30 wtpm, no melt properties by branching will be obtained.
- The amounts of such heterogeneous structural units can readily be obtained by hydrolyzing the produced aromatic polycarbonate with an alkali, and subjecting it to e.g. high performance liquid chromatography (HPLC) or gel permeation chromatography (GPC), and the structural units of the above formulae (1) to (5) are detected as compounds of the following formulae (9) to (13),

respectively, e.g. by high performance liquid chromatography (HPLC) after hydrolysis with an alkali:

【Ka 13】



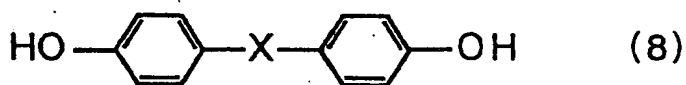
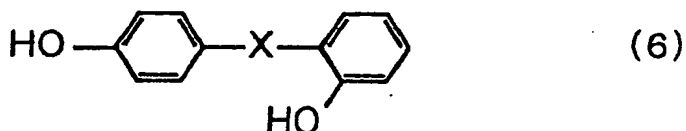
5 The structural units of the above formulae (1) to (5) are estimated to be due to heterogeneous structures produced as by-products mainly along with a transfer reaction or the like in the process for producing an aromatic polycarbonate by transesterification.

Selection of aromatic dihydroxy compound

In order to obtain the above specific branched aromatic polycarbonate, it is important to select an appropriate material aromatic dihydroxy compound when a
5 carboxylic acid diester and an aromatic dihydroxy compound are reacted to produce a branched aromatic polycarbonate.

Namely, it is preferred to select a 4,4'-bisphenol compound of the following formula (8) containing a 2,4'-
10 bisphenol compound of the following formula (6) in an appropriate amount practically a 4,4'-bisphenol compound of the following formula (8) in which the compound of the formula (6) formed as a by-product is remained in an appropriate amount without completely being removed at
15 the time of purification:

【Ka 14】



In the formulae (6) and (8), X is a single bond, a
C₁₋₈ alkylene group, a C₂₋₈ alkylidene group, a C₅₋₁₅
20 cycloalkylene group, a C₅₋₁₅ cycloalkylidene group or a member selected from bivalent groups represented by -O-,
-S-, -CO-, -SO- and -SO₂-.

Specific examples of the 2,4'-bisphenol compound of the formula (6) include 2,4'-dihydroxydiphenyl-1,1-methane, 2,4'-dihydroxydiphenyl-1,1-ethane, 2,4'-dihydroxydiphenyl-2,2-propane, 2,4'-dihydroxydiphenyl-2,2-butane, 2,4'-dihydroxydiphenyl-2,2-octane, 2,4'-dihydroxydiphenyl-1,1-cyclopentane, 2,4'-dihydroxydiphenyl-1,1-cyclohexane, 2,4'-dihydroxydiphenyl ether, 2,4'-dihydroxydiphenylsulfide, 2,4'-dihydroxydiphenylsulfoxide and 2,4'-dihydroxydiphenylsulfone.

The 2,4'-bisphenol compound to be remained varies depending upon the type of the material 4,4'-bisphenol compound, but in the case of bisphenol A, preferred is 2,4'-dihydroxydiphenyl-2,2-propane (hereinafter referred to as "2,4'-bisphenol A" or "2,4'-BPA").

However, it is not difficult to obtain a 4,4'-bisphenol compound in which a 2,4'-bisphenol compound is remained in an appropriate amount, since the 2,4'-bisphenol compound of the above formula (6) is usually produced as a by-product at the time of producing the 4,4'-bisphenol compound of the above formula (8).

For example, when phenol and acetone are reacted in the presence of an acid catalyst such as a strongly acidic ion exchange resin to produce bisphenol A, a reaction mixture containing 2,4'-bisphenol A as a by-product is obtained, and bisphenol A, 2,4'-bisphenol A and the like are purified and separated from the reaction

mixture. Namely, an excess amount of phenol is added to the reaction mixture and dissolved, then the solution is cooled to precipitate an adduct (adduct crystals) comprising bisphenol A and phenol in a molar ratio of 1:1.

5 The precipitated adduct crystals are separated from a mother liquor by e.g. filtration or centrifugal separation, and corresponding to the 2,4'-bisphenol compound to be remained, an operation of re-dissolution in e.g. phenol, crystallization and separation is

10 repeatedly carried out to obtain bisphenol A with an intended purity.

The appropriate amount of the 2,4'-bisphenol compound to be remained varies depending upon the desired contents of the structural units of the formulae (1) to

15 (3) contained in the main chain of the branched aromatic polycarbonate as the product, but experientially it is better that the amount of the 2,4'-bisphenol compound is usually within a range of from 100 to 10,000 wtppm, preferably from 120 to 9,000 wtppm, based on the 4,4'-

20 bisphenol compound. If its amount is smaller than the above range, the degree of branching tends to be inadequate, whereby fluidity under a high load will not increase, and on the other hand, if its amount is too large, branching tends to proceed excessively, gelation

25 tends to proceed, and molding of the polymer tends to be difficult, such being unfavorable.

To the aromatic polycarbonate of the present

invention, a conventional additive such as a heat resistant stabilizer, an ultraviolet absorber, a releasing agent, a coloring agent, an antistatic agent, a slipping agent, an antiblocking agent, a lubricant, an anti-fogging agent, natural oil, synthetic oil, wax, an organic filler or an inorganic filler may be added. Such an additive may be added to a resin in a molten state, or it may be added after a once pelletized resin is re-melted.

10 **【Examples】**

Now, the present invention will be explained in detail with reference to Examples, however, the present invention is not limited to such specific Examples.

In the following Examples and Comparative Examples, analysis of bisphenol A used and the obtained aromatic polycarbonate was carried out by the following measuring methods.

(1) Amount of 2,4'-bisphenol A in bisphenol A

Using high performance liquid chromatography (HPLC), measurement was carried out at a detection wavelength of 280 nm. The content was obtained from an analytical curve of 2,4'-bisphenol A.

(2) Contents of structural units of the above formulae (1) to (5)

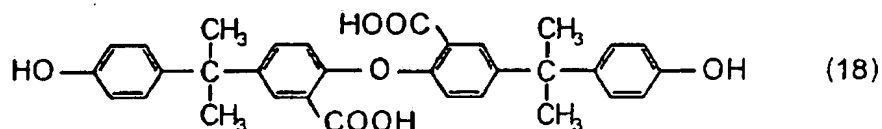
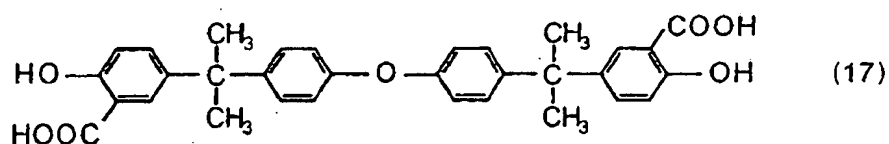
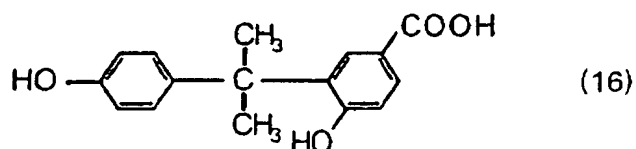
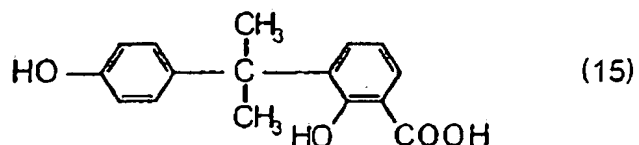
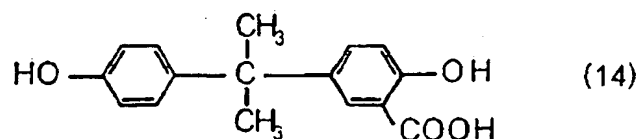
25 1 g of the aromatic polycarbonate (sample) was dissolved in 100 ml of methylene chloride, 18 ml of a 28% sodium methoxide methanol solution and 80 ml of methanol

were added thereto, and 25 ml of pure water was further added thereto, followed by stirring at room temperature for 2 hours for complete hydrolysis. Then, 1N hydrochloric acid was added thereto for neutralization, and a methylene chloride layer was separated to obtain a hydrolyzate.

0.05 g of the hydrolyzate was dissolved in 10 ml of chloroform, and measurement was carried out by using high performance liquid chromatography (HPLC).

In the liquid chromatography, the structural units of the above formulae (1) to (5) are detected as compounds of the following formulae (14) to (18), and accordingly they were identified in comparison with the standard products. Further, the contents of the respective structural units were calculated from the respective peak areas relative to the peak area of bisphenol A in a prepared analytical curve of bisphenol A. The detection wavelength used was 280 nm.

【Ka 15】



(3) Viscosity average molecular weight

5 The intrinsic viscosity $[\eta]$ of the aromatic polycarbonate (sample) in methylene chloride at 20°C was measured by using a Ubbellohde's viscometer, and obtained from the following formula:

$$[\eta] = 1.23 \times 10^{-4} \times (\text{Mv})^{0.83}$$

10 (4) Hue (YI) and residence stability (heat resistant hue YI)

A molded product was obtained from the aromatic polycarbonate (sample) by using an injection machine under the following conditions.

Tristimulus values XYZ as absolute values of color were measured by means of a color tester (SC-1-CH manufactured by SUGA TEST INSTRUMENTS Co., Ltd.) with respect to a press sheet in a size of 100 mm × 100 mm × 3 mm thickness, at 280°C for YI measurement or at 360°C at fifth shot with a residence of 10 minutes for residence stability measurement, and the YI value as an index of yellowness was calculated from the following relational expression:

$$YI = (100/Y) \times (1.28 \times X - 1.06 \times Z)$$

The higher the YI value, the more the sample is colored.

(5) MI and degree of branching (MIR)

Sample weights (g) of the aromatic polycarbonate (sample) extruded at 260°C for 10 minutes under loads of 21.6 kg and 2.16 kg, respectively, were measured in accordance with a method for testing melt mass flow rate (MFR) in JIS K7210, and taken as MI (21.6 kg) and MI (2.16 kg), respectively. The higher these values, the higher the fluidity.

Further, the degree of branching (MIR) is represented by the ratio of MI (21.6 kg)/MI (2.16 kg) as measured above. The higher this value, the higher the degree of branching.

EXAMPLE 1

In accordance with a conventional method, phenol and acetone were reacted in the presence of a strongly acidic ion exchange resin, an excess amount of phenol was added
5 to the obtained bisphenol A reaction mixture, and the reaction mixture was dissolved and then cooled to precipitate an adduct (adduct crystals) of bisphenol A and phenol. The precipitated adduct was separated from a mother liquor by filtration, and subjected to dissolution
10 in phenol, precipitation and separation until bisphenol A containing 200 wtppm of 2,4'-bisphenol A was obtained.

Diphenyl carbonate and the obtained bisphenol A were mixed and prepared to a certain molar ratio (DPC/BPA=1.040) in an atmosphere of nitrogen gas, and the
15 obtained melt liquid was continuously supplied to a first vertical stirring polymerization tank having a capacity of 100 L, controlled to 220°C and 1.33×10^4 Pa at a flow rate of 88.7 kg/hr through a material introduction tube, and the liquid level was kept constant while controlling
20 the bulb aperture installed at the polymer discharge line at the bottom of the tank so that the average residence time would be 60 minutes. Further, a sodium hydroxide aqueous solution as the catalyst was continuously
supplied in a proportion of 1.0×10^{-6} mol per 1 mol of
25 bisphenol A, simultaneously with initiation of supply of the above mixture.

The polymer liquid discharged at the bottom of the

tank was sequentially and continuously supplied to second and third vertical stirring polymerization tanks having a capacity of 100 L and a fourth horizontal polymerization tank having a capacity of 150 L, and drawn out from the polymer discharge port at the bottom of the fourth polymerization tank. Then, the polymer in a molten state was introduced to a twin screw extruder, butyl p-toluene sulfonate (4 times the molar quantity of the cesium carbonate used as the catalyst) was continuously kneaded therewith, and the mixture was formed into a strand through a die and cut by a cutter to obtain pellets. The reaction conditions in the second to the fourth polymerization tanks were such that the second polymerization tank (240°C, 2.00×10^3 Pa, 75 rpm), third polymerization tank (270°C, 66.7 Pa, 75 rpm) and the fourth polymerization tank (275°C, 26.7 Pa, 5 rpm), respectively, and the conditions were set so that the temperature became high, the degree of vacuum became high and the stirring rate became low along with progress of the reaction. Further, the liquid level was controlled so that the average residence time would be 60 minutes in each of the second to fourth polymerization tanks during the reaction, and at the same time, phenol formed as a by-product was distilled off.

A polycarbonate having a viscosity average molecular weight of 24,400 was obtained, and the contents of the structural units of the above formulae (1) to (5), the

hue (YI), the residence stability, MI and the degree of branching (MIR) were measured. The results are shown in Table 1.

EXAMPLES 2 and 3 and COMPARATIVE EXAMPLE 1

5 Polymerization was carried out in the same manner as in Example 1 to produce an aromatic polycarbonate except that in Example 1, bisphenol A as identified in Table 1 was used. The results are shown in Table 1.

COMPARATIVE EXAMPLE 2

10 Polymerization was carried out in the same manner as in Comparative Example 1 to produce an aromatic polycarbonate except that in Comparative Example 1, 1,1,1-tris(4-hydroxyphenyl)ethane (THPE) as a branching agent was added in an amount of 0.3 mol% to bisphenol A.
15 The results are shown in Table 1.

【Table 1】

	Ex. 1	Ex. 2	Ex. 3	Comp. Ex. 1	Comp. Ex. 2
Amount of 2,4'-bisphenol A in bisphenol A	200	500	1,000	80	80
Content of structural units of the formula (1)	3,200	4,000	5,400	600	600
Content of structural units of the formula (2)	40	120	200	5	5
Content of structural units of the formula (3)	60	150	320	10	10
Total content of structural units of formulae (4) and (5)	100	520	1,040	3	3
Mv	24,400	24,500	24,500	24,200	24,300
YI	1.6	1.7	1.8	1.7	3.1
Residence stability	6.7	6.8	6.9	6.6	12.5
MI (21.6 kg)	18.2	20.6	22.2	10.2	8.1
MI (2.16 kg)	0.9	0.9	0.9	0.8	0.5
Degree of branching: MIR	20.2	22.9	24.7	12.8	16.2

【Effects of the Invention】

According to the present invention, an aromatic polycarbonate has improved fluidity under a high load,
5 and has a favorable hue, and accordingly it is suitable for processing by extrusion and injection molding, particularly for application as a hollow part and a large panel by blow molding which requires a material having a high melt strength and excellent shape-holding properties
10 of an extruded product.

【TYPE OF DOCUMENT】 ABSTRACT

【SUMMARY】

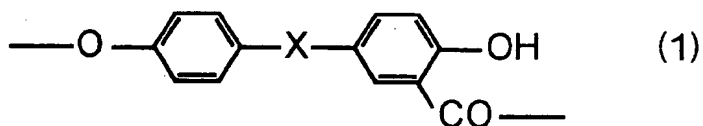
【OBJECT】

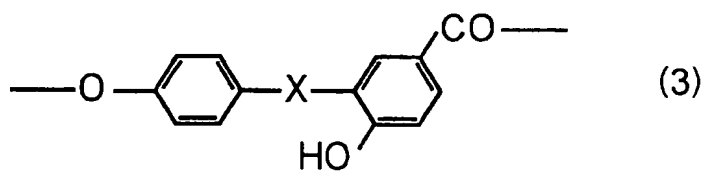
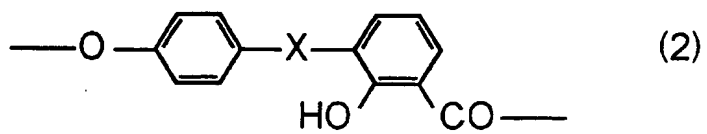
It is to provide a branched aromatic polycarbonate
5 excellent in hue and excellent in melt properties such as
melt strength.

【MEANS OF SOLVING PROBLEMS】

A branched aromatic polycarbonate obtained by
transesterification and having a viscosity average
10 molecular weight of at least 16,000, wherein the amount
of structural units of the following formula (1)
contained in its main chain is within a range of from
3,000 to 10,000 wtpm, and the amounts of structural
units of the following formulae (2) and (3) contained in
15 its main chain are within a range of from 30 to 5,000
wtpm, respectively:

【Ka 1】





【SELECTED FIGURE】

No Selected Figure